Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (Rev. 5-93)

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NO **H 4388 PCT/US**

U S APPLICATION NO (if known sec 17 CFR 1 5) **10/069409**

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/07975	**August 16, 2000**	**August 24, 1999**

TITLE OF INVENTION
MICROWAVE BONDING

APPLICANT(S) FOR DO/EO/US
Christian Kirsten, Dieter Dausmann, Uwe Franken, and Nikolaus Mathes

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information.

1. ■ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. ☐ This a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U S.C. 371

3. ☐ This express request to begin national examination procedures (35 U S C 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U S C 371(b) and PCT Articles 22 and 39 (1)

4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date

5. ■ A copy of the International Application as filed (35 U S. C. 371(c)(2)).
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ■ has been transmitted by the International Bureau
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).

6. ■ A translation of the International Application into English (35 U.S.C. 371(c)(2))

7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U S C 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ■ have not been made and will not be made

8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C 371(c)(3))

9. ■ An oath or declaration of the inventor(s) (35 U S.C. 371(c)(4)) **UNEXECUTED**

10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5))

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3 28 and 3.31 is included

13. ■ A FIRST preliminary amendment
    ☐ A SECOND or SUBSEQUENT preliminary amendment

14. ☐ A substitute specification.

15. ☐ A change of power of attorney and/or address letter.

16. ☐ Other items or information.:

Version with Markings to Show Changes Made

"Express Mail" mailing label number EL615775349US

U.S. Application No. (If known see CFR 1.60) 10/069409	INTERNATIONAL APPLICATION NO PCT/EP00/07975	ATTORNEY'S DOCKET NUMBER H 4388 PCT/US

17. ■ The following fees are submitted.	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO. **$890.00**		
International preliminary examination fee paid to USPTO (37CFR 1.482) **$710.00**		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2)) .. **$740.00**		
Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. **$1,040.00**		
International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).... . **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890	00
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date 37 (CFR 1.492(e))	$	

Claims	Number filed	Number Extra	Rate		
Total Claims	1-20 =1	0	X 18.00	$	0
Independent Claims	1-3 =1	0	X 84 00	$	00
Multiple dependent claims (s)(if applicable)		0	+ 280 00	$	00
TOTAL OF ABOVE CALCULATIONS ..... =				$ 890	00
Reduction by ½ for filing by small entity, if applicable Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL =				$	00
Processing fee of **$130.00** for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37CFR 1.492(f)) .... +				$	
TOTAL NATIONAL FEE =				$	00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) $40.00 per property +				$	
TOTAL FEES ENCLOSED =				$	890
				Amount to be refunded	$----------
				charged	

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.
b. ■ Please charge my Deposit Account No. **01-1250** in the amount of **$ 890.00** to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. **02-0107**.
c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **01-1250**. A triplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO Henkel Corporation, Law Dept.
2500 Renaissance Blvd., Ste. 200
Gulph Mills, PA 19406.....

Kimberly R. Hild
SIGNATURE

Kimberly R. Hild
NAME ATTORNEY FOR APPLICANT

39,224
REGISTRATION NUMBER

Form PTO 1390 (REV 5-93)

PATENT
Docket No. H 4388 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Kirsten, et al.

International Application No. PCT/EP00/07975
International Filing Date: August 16, 2000

Serial No. To be assigned **Examiner:** To be assigned

Filed: To be assigned **Art Unit:** To be assigned

Title: MICROWAVE BONDING

"Express Mail Post Office to Addressee" service mailing label number EL615775349US

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification (Using the English Translation):

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following paragraph:

Docket No. H4388 PCT/US
PCT/EP00/07975

-- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP00/07975 filed on August 16, 2000, the international application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 199 40 128.4 filed on August 24, 1999.

On page 1, on a separate line after the above inserted paragraph and before line 1, please insert the following header:
-- BACKGROUND OF THE INVENTION -- .

On page 2, on a separate line between lines 20 and 21, please insert the following header: --SUMMARY OF THE INVENTION--.

On page 3, on a separate line between lines 2 and 3, please insert the following header: -- DETAILED DESCRIPTION OF THE INVENTION --.

On page 9, line 1, please delete the heading "CLAIMS" and insert therefor:
-- What is claimed is: --

On a separate page, after page 10, please insert the enclosed Abstract of the Disclosure.

In the Claims

Please cancel Claims 2 to 11, without prejudice.

Docket No. H4388 PCT/US
PCT/EP00/07975

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claim 1 will be pending after entry of the present amendment. Claims 2 to 11 are being canceled without prejudice.

Amendment

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein.

Attached hereto is a marked up version of the changes made to the specification entitled "Version With Markings To Show Changes Made."

No new matter is added by the amendments to the specification.

Docket No. H4388 PCT/US
PCT/EP00/07975

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

Kimberly R. Hild

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February 25, 2002

Henkel Corporation
Law Department
2500 Renaissance Boulevard, Suite 200
Gulph Mills, PA 19406

Docket No. H4388 PCT/US
PCT/EP00/07975

Abstract of the Disclosure

A process for bonding at least two substrates with a hotmelt adhesive using microwave energy is provided. The process includes applying a microwave-activatable primer to a least one of the substrates and applying a hotmelt adhesive to a least one of the substrates. The method also includes pressing the substrates together so that the microwave-activatable primer and the hot melt adhesive are between the substrates, and exposing at least the microwave-activatable primer to microwaves to heat the hotmelt adhesive. The present invention also provides a process for spraying a hot melt adhesive onto a substrate where the hot melt adhesive includes nanoparticles having ferromagnetic, ferrimagnetic, superparamagnetic or piezoelectric properties.

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

On page 9, line 1, the heading "CLAIMS" has been amended as shown below:

[CLAIMS] What is claimed is:

PATENT
Docket No. H 4388 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Kirsten, et al.

International Application No. PCT/EP00/07975
International Filing Date: August 16, 2000

Serial No. 10/069,409
Filed: To be assigned

Examiner: To be assigned
Art Unit: To be assigned

Confirmation No. 3267

Title: MICROWAVE BONDING

"Express Mail Post Office to Addressee" service mailing label number EV 105943565 US

SUPPLEMENTAL PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Claims

Please cancel Claim 1, without prejudice.

Please add the following new claims:

--12. (NEW) A process for bonding substrates with hotmelt adhesive comprising:

(a) providing at least two substrates for bonding together;

(b) applying at least one microwave-activatable primer to at least one of the substrates;

(c) applying at least one hotmelt adhesive to at least one of the substrates;

(d) pressing the at least two substrates together so that the primer and the hotmelt adhesive are between the substrates and exposing at least the microwave-activatable primer to microwaves to heat the hotmelt adhesive; and

(e) cooling the hotmelt adhesive

13. (NEW) The process of claim 12 wherein one of the substrates is porous and the other substrate is porous or nonporous.

14. (NEW) The process of claim 13 wherein at least one of the substrates is a porous woven or nonwoven fibrous substrate selected from leather or a textile.

15. (NEW) The process of claim 12 wherein the microwave-activatable primer comprises a mixture of at least two different microwave-active additives in a quantity sufficient to heat the hotmelt adhesive to where it flows.

16. (NEW) The process of claim 15 wherein the two microwave-active additives differ in at least one property selected from size, shape, electrical conductivity or thermal conductivity, or combinations thereof.

17. (NEW) The process of claim 12, wherein the hotmelt adhesive is thermoplastic or reactive and contains no microwave-activatable additives.

18. (NEW) The process of claim 12, wherein the hotmelt adhesive is applied in a solid or molten state.

19. (NEW) The process of claim 18 wherein the hotmelt adhesive is applied in the form of a film, net or powder.

20. (NEW) The process of claim 18 wherein the hotmelt adhesive is applied as a melt to the substrate.

21. (NEW) The process of claim 18 wherein the hotmelt adhesive is applied by spraying the hotmelt adhesive onto at least one of the substrates.

22. (NEW) The process of claim 12 wherein the applied microwave-activatable primer is exposed to electromagnetic fields of 1 Hz to 100 GHz to improve wetting or penetration or both of the hotmelt adhesive.

23. (NEW) The process of claim 12 wherein the substrates having the liquid hotmelt adhesive and the microwave-activatable primer in between are pressed together under a pressure ranging from 0.5 bar to 6 bar for a time period ranging from 5 seconds to 20 minutes.

24. (NEW) The process of claim 23 wherein the substrates are pressed together under a pressure ranging from 2 bar to 5 bar for a time period ranging from 10 seconds to 30 seconds.

25. (NEW) The process of claim 12, wherein the microwave-activatable primer is exposed to microwaves that heat the primer and not the substrates.

26. (NEW) The process of claim 12 wherein after exposing the microwave -activatable primer to the microwaves, the substrates remain pressed together at least until after the hotmelt adhesive begins to solidify.

27. (NEW) The process of claim 26 wherein the substrates remain pressed together at least until the hotmelt adhesive has cooled to a temperature of about 30°C.

28. (NEW) The process of claim 12 wherein the substrates are components of a shoe and the process is part of an in-line process for making shoes.

29. (NEW) A process for applying hotmelt adhesive comprising spraying hotmelt adhesive to at least one substrate wherein the hotmelt adhesive comprises nanoscale particles having ferromagnetic, ferrimagnetic, superparamagnetic or piezoelectric properties.

30. (NEW) The process of claim 29 wherein the substrate is a component of a shoe. --

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claims 12 to 30 will be pending after entry of the present amendment. Claim 1 is being canceled without prejudice.

Amendment

New Claims 12 to 30 replace original claims 1 to 11, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
12	page 2, lines 21 to 30
13	page 1, lines 1 to 3
14	original claim 2
15, 16	original claim 3
17	page 3, lines 15 to 19
18, 19, 20, 21	original claim 5
22	page 5, lines 7 to 9
23, 24	original claim 7
25	original claim 8
26	page 5, lines 23 to 27
27	original claim 9
28	original claim 10
29, 30	page 5, line 27 to page 6, line 9, page 1, lines 1 to 3

No new matter is added by the new claims.

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

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May 31, 2002

Henkel Corporation
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Microwave Bonding

This invention relates to a process for bonding porous and/or nonporous substrates with hotmelt adhesives, more particularly in shoe manufacture.

Requirements and specifications for an adhesive in shoe manufacture are described in **EN 522** and **EN 1392**. A particularly important requirement is a high spotting tack which ensures exact positioning, for example of the sole on the shoe base. In addition, the quality/strength of the bond presupposes good penetration/wetting of the substrates to be bonded, particularly where they are porous and above all fibrous. These requirements conflict with one another, particularly where hotmelt adhesives are used. The prior art is based either on amorphous systems or crystalline formulations. Whereas amorphous hotmelt adhesives show adequate spotting tack, their penetration/wetting is unsatisfactory. Where crystalline systems are used, good penetration is generally present whereas their spotting tack for positioning the shoe sole is inadequate. Although amorphous or crystalline hotmelt adhesives can be optimized in regard to the described problems, such improvements are only ever achieved at the expense of the other requirement described above. Optimal spotting tack coupled with optimal penetration/wetting cannot be achieved solely by formulation in accordance with the prior art.

In known processes, the above-mentioned difficulties can only be overcome by additional and expensive process steps. **DE 19504007**, for example, describes the pre-heating or post-heating of substrates to improve the penetration of an amorphous hotmelt adhesive. An alternative way and, in many cases, the only way of obtaining a high-quality bond is the additional application of a primer and/or adhesive layer for carrying out contact bonding (two-way process). In many cases, this means that the

objective of solventless bonding cannot be achieved.

WO 99/24520 describes a microwave-activatable adhesive which, besides its polymers, additionally contains a mixture of two components which are receptive to microwaves and which - in terms of size, shape and conductivity - are selected to increase the absorption of the microwaves in the polymeric composition. In order to bond wood, plastics and semiconductors to one another, the adhesive is said to be applied to one or both substrates in known manner, for example by spraying, and then exposed to microwave radiation, the adhesive forming a bond. The disadvantage of this adhesive is that it cannot be accurately or constantly applied by spraying and is therefore unsuitable for certain applications, for example in shoemaking for bonding soles.

Against the background of this prior art, the problem addressed by the present invention was to provide a process for bonding porous and nonporous materials where the strength requirements would be safely fulfilled and spray application of the adhesive would be unproblematic.

The solution to this problem is defined in the claims and consists essentially in the fact that the primer and not the adhesive contains additives which are receptive to microwaves and with which the adjacent adhesive layer can be activated.

Accordingly, the present invention relates to a process for bonding porous and/or nonporous substrates with adhesives, more particularly hotmelt adhesives, in which

a) a microwave-activatable primer is applied to at least one substrate,

b) an adhesive, more particularly a hotmelt adhesive, is applied to at least one substrate,

c) both substrates with the primer and the adhesive or the hotmelt adhesive in between are exposed to microwaves and at the same time pressed together and

d) the microwave-heated adhesive is left to set.

Preferred embodiments of the invention can be found in the dependent claims.

So far as the microwave-active additives are concerned, reference is specifically made to **WO 99/24520** of which the disclosure is hereby included as part of the disclosure of the present invention. In addition, however, it is pointed out that the primer may also contain nanoscale microwave-active additives. In this case, one component is sufficient.

So far as the bonding process is concerned, reference is made to **WO 99/24498** of which the disclosure is also included as part of the subject matter of the present application.

The essential aspects of the present invention are discussed in the following.

The process according to the invention resolves the described limitation in the bonding of shoes.

Accordingly, the process according to the invention is based on the use of thermoplastic and/or reactive adhesive systems which can be selectively activated by electromagnetic radiation through the primary layer. Activation is based on locally defined heating of the primer layer and hence the adjacent adhesive layer. The bonded substrates are heated only slightly and ideally not at all, but at all events more slowly than the modified adhesive system with a microwave-active primer layer and hence are subjected to little or no heat stress. The activation of the adhesive layer through the primer layer in accordance with the invention differs significantly from the conventional activation processes presently used in the shoe industry (for example IR radiation, circulated hot air).

The locally defined heating of the adhesive layer through the primer layer in accordance with the invention is made possible by the modification of standard primers with suitable "signal receivers" which absorb electromagnetic energy, as described in **WO 93/02867**. For shoe adhesives, such signal receivers are, for example, quartz, tourmaline,

barium titanate, lithium sulfate, potassium (sodium) tartrate, ethylenediamine tartrate, ferroelectric materials of perovskite structure and, above all, lead zirconium titanate. Where magnetic alternating fields are used, any ferrimagnetic, ferromagnetic or superparamagnetic materials are basically suitable, more particularly the metals aluminium, cobalt, iron, nickel or alloys thereof and metal oxides of the n-maghemite type (γ-Fe_2O_3) and the n-magnetite type (Fe_3O_4), ferrites with the general formula $MeFe_2O_4$, where Me stands for divalent metals from the group consisting of copper, zinc, cobalt, nickel, magnesium, calcium or cadmium. Carbon blacks and carbon fibers are also suitable. In addition, it essentially contains the known components for primers, for example chloramine, chlorinated polyolefins, polychloroprene or polyurethane. These components are preferably selected according to the hotmelt adhesive components and the substrates.

The primer is preferably applied to at least one substrate in the form of a solution or dispersion.

Suitable adhesives are, in principle, any known adhesives providing they are sprayable, more particularly sprayable hotmelt adhesives. In principle, they may contain all the usual polymers. Examples of thermoplastically softenable adhesives are hotmelt adhesives based on ethylene/vinyl acetate copolymers, polybutenes, styrene/isoprene/styrene and styrene/butadiene/styrene copolymers, thermoplastic elastomers, amorphous polyolefins, linear thermoplastic polyurethanes, copolyesters, polyamide resins, polyamide/EVA copolymers, polyaminoamides based on dimer fatty acids, polyester amides or polyether amides. Other suitable adhesives are, in principle, the known two-pack adhesives based on one- or two-component polyurethanes, one- or two-component polyepoxides, silicone polymers (one or two components), the silane-modified polymers described, for example, in **G. Habenicht, "Kleben: Grundlagen, Technologie, Anwendungen", 3rd Edition, 1997, Chapter 2.3.4.4**. The

(meth)acrylate-functional two-pack adhesives based on peroxidic hardeners, anaerobic curing mechanisms, aerobic curing mechanisms or UV curing mechanisms are also suitable as the adhesive matrix.

The adhesives are preferably low-solvent types, i.e. they contain less than 1% by weight of organic materials boiling at temperatures below 200°C.

Suitable frequencies for the selective heating of the primer layer are any electromagnetic fields from 1 Hz to 100 GHz. Magnetic alternating fields with frequencies from 10 KHz to 10 GHz are particularly suitable.

The process according to the invention counters the known difficulties involved in the use of thermoplastic and/or reactive hotmelt adhesives by the use of a modified adhesive system - applied to one side - of a primer and a hotmelt adhesive with optimized spotting tack, optionally with the additional aid of conventional activation processes, to facilitate exact positioning, for example of the sole on the shoe base or an inner sole. The composite structure thus produced is then pressed in a device suitable for the process according to the invention and is activated by electromagnetic energy in that state, as described above. In this way, the adhesive layer adjacent the primer layer is crosslinked in a state for optimal penetration/wetting through the selective heating of the primer layer and hence the adjacent adhesive layer. In this way, the standards laid down in EN 522 and EN 1392 are achieved or surpassed.

In another embodiment of the process according to the invention, the bonded structure is cooled in the pressed state after activation. The advantage of this is that it eliminates the risk of unwanted opening of the bonded structure - still warm after activation - through recovery forces at work in the shoe material.

The present invention also relates to a process for establishing adhesive bonds by means of electrical, magnetic or electromagnetic alternating fields, the adhesive layer containing nanoscale particles which

directly heat the adhesive layer under the influence of these alternating fields. The object of heating the adhesive layer in this way is to increase the strength of the bonds through better wetting or penetration by the heated adhesive, more particularly the hotmelt adhesive. The nanoscale particles act as fillers with "signal receiver" properties so that energy in the form of electromagnetic alternating fields is purposefully introduced into the adhesive bond. The introduction of energy into the adhesive results in a considerable local increase in temperature so that the viscosity is reduced.

The process according to the invention is distinguished from the conventional methods of heating by the fact that the heat is generated in the adhesive joint itself and is locally confined thereto and by the fact that the substrate materials to be bonded are subjected to little or no heat stress. The process is very quick and effective because the heat does not have to be introduced into the adhesive joint by diffusion through the substrates. The process according to the invention also considerably reduces heat losses through dissipation or radiation through the substrate so that it is particularly economical. Above all, however, the nanoscale particles at best merely impede but do not prevent spraying of the adhesive melt.

Electrical alternating fields or magnetic alternating fields are suitable for the introduction of energy. Where electrical alternating fields are applied, suitable filler materials are any piezoelectric compounds, for example quartz, tourmaline, barium titanate, lithium sulfate, potassium (sodium) tartrate, ethylenediamine tartrate, ferroelectric materials of perovskite structure and, above all, lead zirconium titanate. Where magnetic alternating fields are used, any ferrimagnetic, ferromagnetic or superparamagnetic materials are basically suitable, more particularly the metals aluminium, cobalt, iron, nickel or alloys thereof and metal oxides of the n-maghemite type (γ-Fe_2O_3) and the n-magnetite type (Fe_3O_4), ferrites with the general formula $MeFe_2O_4$, where Me stands for divalent metals

from the group consisting of copper, zinc, cobalt, nickel, magnesium, calcium or cadmium.

Where magnetic alternating fields are used, nanoscale superparamagnetic particles, so-called single domain particles, are particularly suitable. Compared with the paramagnetic particles known from the prior art, the nanoscale fillers are distinguished by the fact that they have no hysteresis. The result of this is that the dissipation of energy is not produced by magnetic hysteresis losses, instead the generation of heat is attributable to an oscillation or rotation of the particles in the surrounding matrix induced during the action of an electromagnetic alternating field and, hence, ultimately to mechanical friction losses. This leads to a particularly effective heating rate of the particles and the matrix surrounding them.

Nanoscale particles in the context of the present invention are particles with a mean particle size (or a mean particle diameter) of no more than 500 nm and preferably no more than 300 nm. The nanoscale particles to be used in accordance with the invention preferably have a mean particle size of 1 to 40 nm and more preferably 3 to 30 nm. In order to utilize the effects through superparamagnetism, the particle sizes should be no more than 30 nm. The particle size is preferably determined by the UPA (ultrafine particle analyzer) method, for example by laser light back scattering. In order to prevent or avoid agglomeration or coalescence of the nanoscale particles, the particles are normally surface-modified or surface-coated. A corresponding process for the production of agglomerate-free nanoscale particles, for example iron oxide particles, is described in columns 8 to 10 of **DE-A-196 14 136**. Methods for the surface coating of such nanoscale particles for avoiding agglomeration thereof are disclosed in **DE-A-197 26 282**.

The nanoscale materials are added to the adhesive in a quantity of 1 to 30% by weight and preferably 3 to 10% by weight, based on the

composition as a whole.

In principle, any relatively high-frequency electromagnetic alternating field may be used as the energy source for heating the nanoscale particles. For example, electromagnetic radiation of the so-called ISM (industrial, scientific and medical applications) ranges, i.e. frequencies between 100 MHz and about 200 GHz, may be used, cf. inter alia **Kirk-Othmer, "Encyclopedia of Chemical Technology", 3rd Edition, Vol. 15, chapter entitled "Microwave technology"**, for further particulars.

It was pointed out in the foregoing that, where nanoscale particles according to the invention are used, electromagnetic radiation may be used to particular effect. This is clearly reflected in the fact that, even in the low-frequency range of about 50 kHz or 100 kHz up to 100 MHz, virtually any frequency can be used to produce the amount of heat needed to split the adhesive bond matrix in the adhesive matrix. A frequency range of 500 kHz to 50 MHz may advantageously be used. The choice of the frequency may be determined by the equipment available, care naturally having to be taken to ensure that interference fields are not radiated.

The adhesives containing the nanoscale particles may be used with or without primers for bonding porous and/or nonporous substrates because they may readily be applied by spraying.

CLAIMS

1. A process for bonding porous and/or nonporous substrates with hotmelt adhesives, in which

a) a microwave-activatable primer is applied to at least one substrate,

b) a hotmelt adhesive is applied to at least one substrate,

c) both substrates with the primer and the hotmelt adhesive in between are exposed to microwaves and at the same time pressed together and

d) the microwave-heated adhesive is left to cool.

2. A process as claimed in claim 1, characterized in that porous substrates, more particularly fibrous substrates, such as leather or textiles in the form of woven or nonwoven materials, are bonded to other porous substrates or to nonporous substrates.

3. A process as claimed in claim 1, characterized in that the microwave-activatable primer contains a mixture of at least two microwave-active additives differing in size, shape and/or electrical or thermal conductivity in a quantity sufficient to heat the hotmelt adhesive layer to the point where it flows.

4. A process as claimed in claim 1, characterized in that the hotmelt adhesive is thermoplastic or reactive and preferably contains no microwave-activatable additives.

5. A process as claimed in claim 1, characterized in that the hotmelt adhesive is applied in the solid state, for example in the form of a film, a net or in the form of a powder, preferably as a melt, above all by spraying.

6. A process as claimed in claim 1, characterized in that the hotmelt adhesive applied is exposed together with the primer and the substrates to electromagnetic fields of 1 Hz to 100 GHz to improve wetting/penetration.

7. A process as claimed in claim 1, characterized in that the substrates with the liquid hotmelt adhesive and primer in between are pressed together under a pressure of 0.5 to 6 bar and preferably 2 to 5 bar for 5

seconds to 20 minutes and preferably for 10 to 30 seconds.

8. A process as claimed in claim 1, characterized in that, through the choice of suitable microwaves, only the primer is heated and not the substrates.

9. A process as claimed in claim 1,characterized in that, after their microwave treatment, the substrates are pressed together at least until the hotmelt adhesive begins to solidify, more particularly until the hotmelt adhesive has reached a temperature of ca. 30°C.

10. A process as claimed in at least one of claims 1 to 9 for the manufacture of shoes by the in-line method.

11. The use of an adhesive composition, more particularly a hotmelt adhesive, containing nanoscale particles with ferromagnetic, ferrimagnetic, superparamagnetic or piezoelectric properties for spray application.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
1. März 2001 (01.03.2001)

PCT

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— *Mit internationalem Recherchenbericht.*

Zur Erklarung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklarungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: MICROWAVE BONDING

(54) Bezeichnung: MIKROWELLEN-VERKLEBUNG

(57) Abstract: The invention relates to an adhesive system for bonding open-pored and/or non-porous substrates. Said adhesive system consists of a primer that can be activated by microwaves and of an adhesive, in particular, of a hot-melt-type adhesive. The primer contains two additives which differ in size, shape and/or flowability or thermal conductivity, and which are provided in a quantity that is sufficient for heating the hot-melt-type adhesive to a temperature at which it flows. The adhesive can be applied as usual, especially by spraying, by virtue of the fact that the adhesive preferably does not contain any additives that can be activated by microwaves.

(57) Zusammenfassung: Zum Verkleben von offenporigen und/oder nicht porösen Substraten wird ein Klebstoffsystem vorgeschlagen, das aus einem mit Mikrowellen aktivierbaren Primer und einem Klebstoff, insbesondere einem Schmelzklebstoff besteht. Der Primer enthält zwei Zusätze, die sich in Größe, Form und/oder Strom- bzw. Wärmeleitfähigkeit unterscheiden, und zwar in einer Menge die ausreicht, um den Schmelzklebstoff bis zum Fließen zu erwärmen. Da der Klebstoff vorzugsweise keine mit Mikrowellen aktivierbaren Zusätze enthält, kann er wie üblich aufgetragen werden, insbesondere durch Sprühen.

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket Number	H 4388 PCT/US
First Named Inventor	Kirsten, Christian
COMPLETE IF KNOWN	
Application Number	10/069,409
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that
My residence, post office address, and citizenship are as stated below next to my name
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

MICROWAVE BONDING

(Title of the Invention)

the specification of which
☐ is attached hereto
OR
☒ was filed on (MM/DD/YYYY) 08/16/2000 as United States Application Number or PCT International Application Number PCT/EP00/07975 and was amended on (MM/DD/YYYY) (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1 56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
199 40 128.4	Germany	08/24/1999	☐	☐	☒

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below

Application Number(s)	Filing Date (MM/DD/YYYY)	
		☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto

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DECLARATION

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I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designating the United Sates of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112 1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1 56 which became available between the filing date of the prior application and the national or PCT international filing date of this application

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(if applicable)*
	PCT/EP00/07975	08/16/2000	

☐ Additional U S or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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DECLARATION

ADDITIONAL INVENTOR(S) Supplemental Sheet

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